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Development of High Temperature Materials for Solid Propellant Rocket Nozzle Applications

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by

Charles R. Manning, Jr.

Professor

and

LeRoy Honeycutt III

Research Assistant

Department of Materials Engineering
North Carolina State University
Raleigh, North Carolina

INTRODUCTION

This research period has been devoted to the study of tantalum carbide-tungsten fiber composites. Evaluation of this material has been completed as far as weight percent carbon additions and weight percent additions of tungsten fiber. Extensive studies were undertaken concerning Young's Modulus and fracture strength of this material. Also, in-depth analysis of the embrittling effects of the extra carbon additions on the tungsten fibers has been completed.

Contained in this progress report is the complete fabrication procedure for the tantalum carbide-tungsten fiber composites with extra carbon additions. Microprobe and metallographic studies showed the effect of extra carbon on the tungsten fibers, and evaluation of the thermal shock parameter fracture strength/Young's Modulus is included.

FABRICATIONS PROCEDURE

Due to the difference in the densities of carbon and tantalum carbide, each sample was mixed separately. Each constituent was correctly weighed and placed in a container. Mixing of the carbon and tantalum carbide was accomplished by adding acetone to the mixture and creating a slurry. After complete mixing and removal of the acetone by a drying process, the tungsten fibers were added and thoroughly mixed. The total weight of each sample before hot pressing was 25 grams.

Hot pressing was accomplished using the standard procedure described in a previous progress report. However, due to the high melting point of both the carbon and the tantalum carbide, the hot pressing parameters were changed. The pressure used during the hot pressing cycle was increased to 8500 psi and temperature was held at 2300°C as a maximum. A vacuum was maintained at less than 20 microns during the complete hot pressing process.

Previous research done using stabilized hafnium oxide and tungsten fibers had proved the sintering process to begin around 1200°C and be completed at a temperature of 1500°C. Further data from the research done with hot pressing of stabilized zirconia-tungsten composites showed the same results. Since the sintering process is directly related to the density, a study of the sintering temperature during fabrication was undertaken. By measuring the temperature and the amount of die ram movement during the hot pressing cycle, the range for the sintering process was confirmed. The sintering process was found to begin at approximately 1400°C and to be essentially completed at 1750°C.

After completion of the hot pressing cycle each sample was removed from the graphite die and visually inspected for gross fabrication defects. After four to five hot pressed samples were accumulated, they were initially cleaned and milled. This consisted of grinding the surfaces with silicon-carbide polishing belts (80 grit) and mounting the specimens on parallel milling blocks. The parallel ends on the samples were produced by milling each sample while attached to the parallel blocks with a horizontal milling machine using a diamond grinding wheel. After the milling of one end of the samples was completed, the samples were turned and final milling of the second end was accomplished. With careful mounting and initial cleaning a specimen can be produced that has the final configuration of a right cylinder. The fabrication of a sample with this final configuration is essential to the generation of reproducable Young's Modulus and fracture strength data.

THERMAL SHOCK PARAMETERS

The physical parameters governing the thermal shock resistance are the Young's Modulus and fracture strength. When evaluating specimens composed of the same initial ingredients, only varying the weight percent of the ingredients, the thermal shock resistance parameter is

$$T.S.R. = {}^{\sigma_{fs}}/E$$

This equation can be used when working with only one material, and it assumes that the thermal expansion of the separate components are compatible. Review of the literature indicates the following data:

Component	Thermal Expansion/^{o}F
TaC	4.1×10^{-6}
W	2.5×10^{-6}
C	$1.5\text{-}2.2 \times 10^{-6}$

This data indicates that the tungsten fibers will be in tension during a increase in temperature and in compression during a decrease in temperature. This statement is also true for carbon. Early research done with the thermal shock resistance of the refractory carbides indicated that additions of carbon increased their thermal shock resistance. Since the thermal expansion data indicates that both tungsten and carbon will be in compression during cooling when incorporated in a tantalum carbide matrix, they will act as a medium for stress relief.

To obtain the data needed for the thermal shock parameter, the following procedure was used. Each sample was characterized by the weight percent tungsten fibers it contained. After final milling and the generation of parallel surfaces on the ends of each sample was completed, SR-5 strain gages (BLH Manufacturers) were mounted on flat surfaces perpendicular to the parallel ends. The recommended adhesive, Eastman 910, was used to attach the strain gages. Electrical wire was soldered to the strain gage leads and electrical conductivity checked by use of a Volt-Ohm meter to insure good electrical contact.

Each sample was mounted in a compression testing machine and the strain gage leads connected to a strain gage indicator. Load was applied and released at a rate that allowed accurate strain readings. The applied load and corresponding strain were recorded and repeated until the readings were linear and reproducable for three complete consecutive cycles.

The Young's Modulus for both the 3 weight percent and the 5 weight percent specimens is given in Figure 1. From this data the decrease in Young's Modulus at an addition of between 1.5 and 2.0 weight percent carbon is evident. This decrease in Young's Modulus follows the same trend that was found in studies on stabilized Hafnium oxide-tungsten composites. This sudden decrease in Young's Modulus usually indicates an increase in the thermal shock resistance parameter if the fracture strength of the material is decreasing at a slower rate. Figure 2 gives the fracture strength of both the 3 w/o and 5 w/o tungsten fiber addition samples. The drop in fracture strength as the content of carbon increased was expected. This decreasing trend in fracture strength can be predicted from either the rules of mixtures or the inverse rule of mixtures given respectively as:

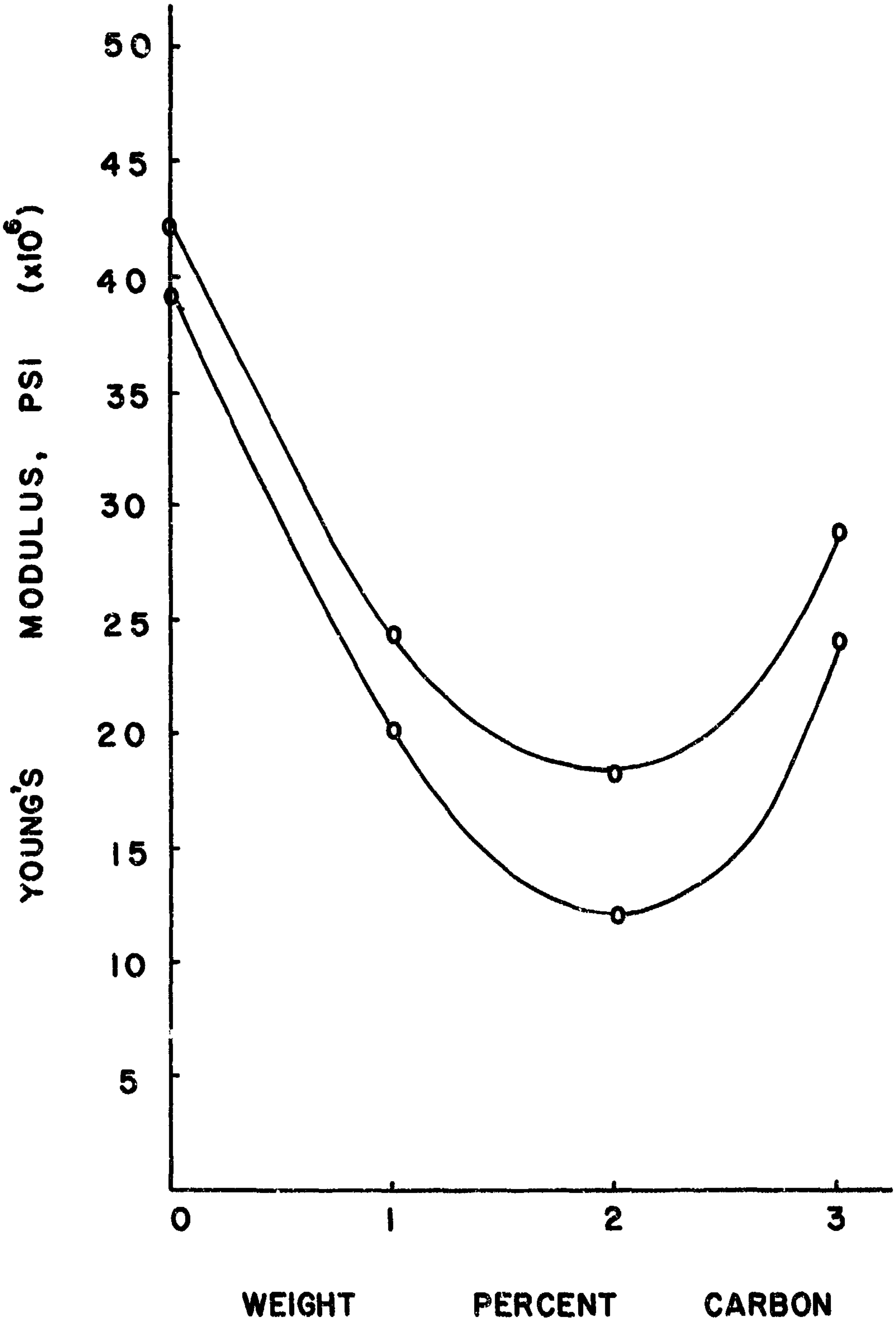


Figure 1. Young's Modulus versus weight percent carbon additions for 5 w/o tungsten fiber (upper line) and 3 w/o tungsten fiber samples.

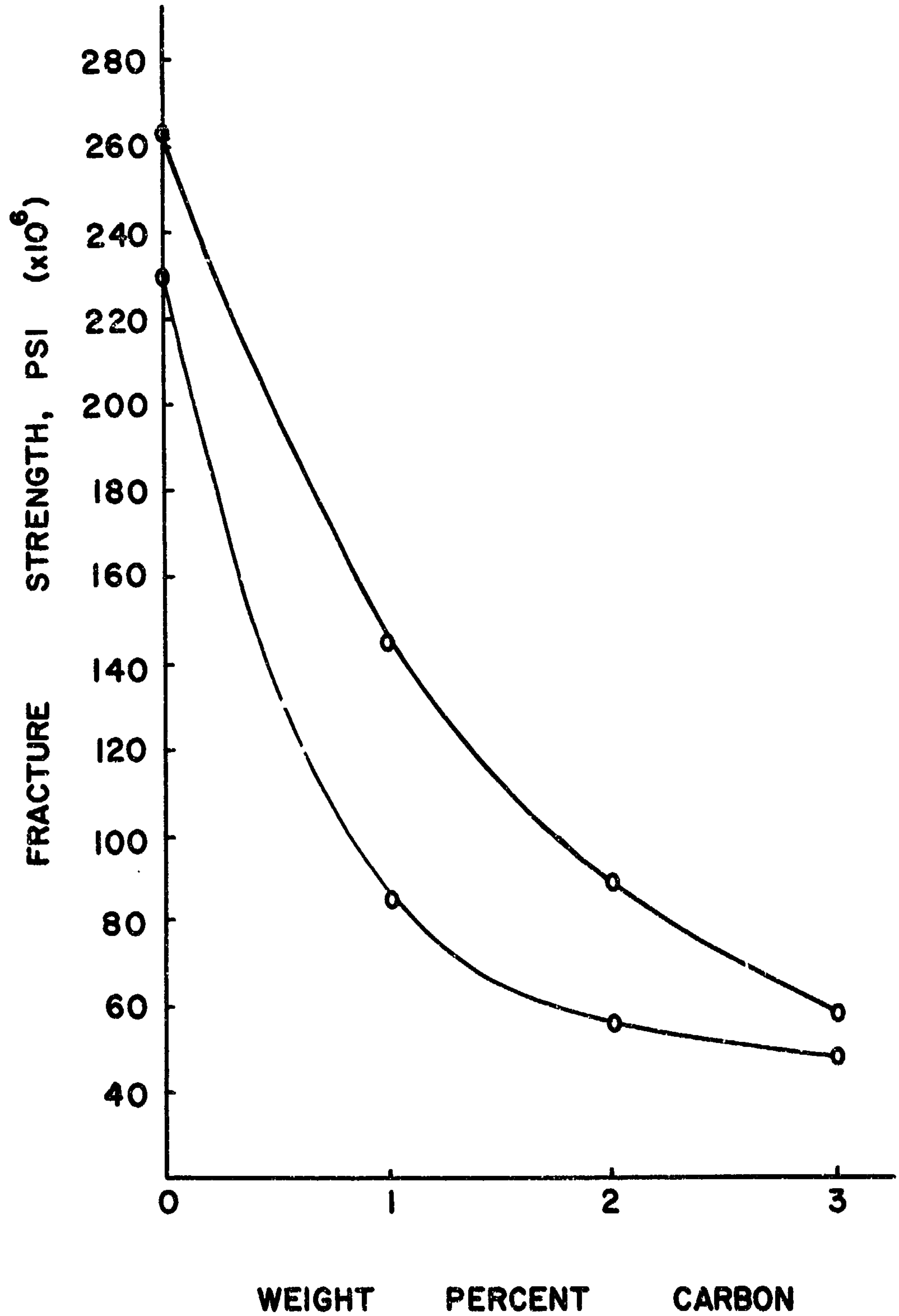


Figure 2. Fracture strength (compression) versus weight percent carbon additions for 3 w/o tungsten fiber (upper line) and 5 w/o tungsten fiber samples.

$$F_c = F_a V_a + F_b V_b + F_e V_e$$

$$\frac{1}{F_c} = \frac{V_a}{F_a} + \frac{V_b}{F_b} + \frac{V_e}{F_e}$$

where

F_c : Fracture strength of composite

F_a : Fracture strength of TaC

F_b : Fracture strength of C

F_e : Fracture strength of tungsten fibers

V_a, V_b, V_e : Respective volume percent present in specimen

The compressive fracture strengths given in Figure 2 are very high for the 3 w/o and 5 w/o tungsten samples. This was attributed to very high densities, greater than 97% theoretical density, and to the lack of any fabrication defects in these samples. This graph predicts the trend of the fracture strength to be decreasing as the weight percent of carbon addition is increased.

The thermal shock resistance parameter is given in Figure 3. This graph was generated from the data given in Figures 1 and 2 by use of the before mentioned equation. This data predicts that the best combination of material is 96 w/o TaC, 1 w/o C, and 3 w/o W fibers. The most important result is found that the thermal shock resistance of a composite material is not based only on its fracture strength.

The difference in the trend of the thermal shock parameters for the specimens containing 3 w/o and 5 w/o tungsten fibers becomes apparent when comparing the rate of decrease of their fracture strength and Young's Modulus. The fracture strength of the specimens containing

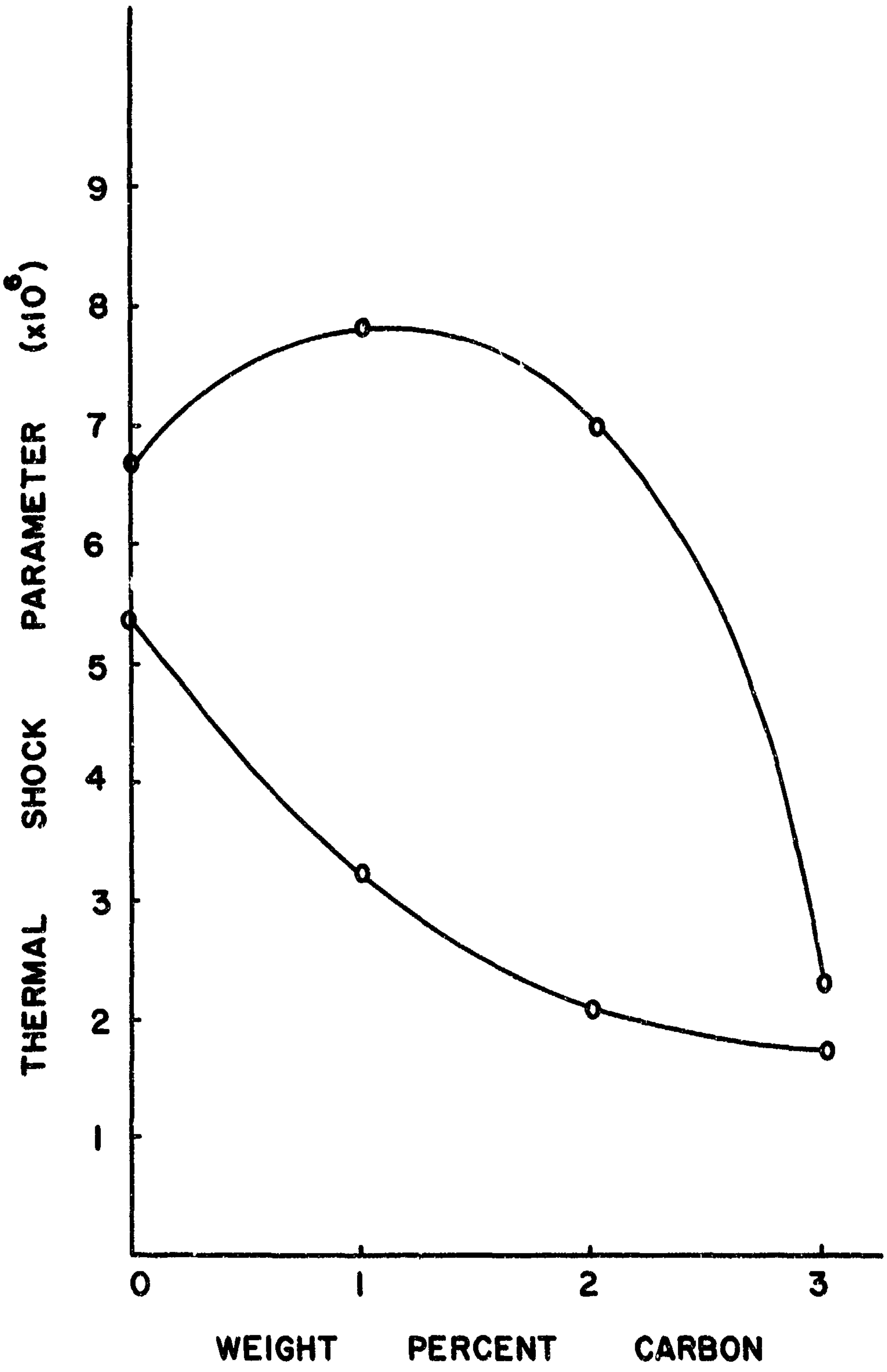


Figure 3. Thermal shock parameter versus weight percent carbon additions for 3 w/o tungsten fiber (upper line) and 5 w/o tungsten fiber samples.

5 w/o tungsten fibers is decreasing at a rate faster than their modulus. This combination of fracture strength and Young's Modulus will produce a decreasing thermal shock parameter with increasing additions carbon.

THERMAL SHOCK TESTING

Thermal shock testing was done on the specimens in the 0 w/o, 3 w/o, and 5 w/o tungsten series. In each particular series, the carbon weight percent addition varied from 0 w/o to 3 w/o. For each composition two samples were thermal shock tested. This testing consisted of exposing the sample to an acylene-oxygen flame for five minutes and quenching in a room temperature water bath. One complete cycle consisted of the heating and quenching with visual inspection between each cycle. The acylene-oxygen flame coupled with the water quenching produce a ΔT (change in temperature) of approximately 1800°C. Although it is known that the ΔT that this material will have to sustain will be approaching 3000°C, this test reduces the number of samples, with inferior physical properties to be exposed to plasma thermal shock tests.

From the data generated by thermal shocking, it has become apparent that the tantalum-tungsten fiber, plus free carbon composites, has to withstand the ΔT of greater than 2800°C needed for a solid propellant rocket nozzle material. The addition of both tungsten fibers and free carbon will be necessary if TaC is used. This statement has been verified by actual thermal shock testing at a ΔT of 1800°C. Samples containing only TaC broke after exposure to four thermal shock cycle. Samples containing TaC plus 3 w/o free carbon fractured after six complete cycles. Samples containing TaC and tungsten fibers showed evidence of severe cracking but maintained their integrity after six complete thermal shock cycles. Samples containing TaC as the matrix material, with both tungsten fibers and free carbon additions, showed no evidence of cracking or loss of specimen integrity.

The ability of TaC specimens containing both tungsten fibers and free carbon additions t withstand repeated thermal shock testing at a ΔT of 1800^oC supports the following statements. To withstand a temperature difference of greater than 2800^oC, the addition of tungsten fibers to insure material integrity and the addition of free carbon to facilitate a stress relieving process will be necessary. Although the tungsten fibers have the ability to relieve some stress through their inherit ductility, their main purpose will be to reduce the energy associated with crack propagation by forcing the cracks to change direction. The low Young's Modulus of carbon (1.3×10^6 psi) indicates it will be the main stress relieving medium during thermal shock.

DENSITY OF HOT PRESSED TaC COMPOSITES

The density of a material has been directly related to the materials strength. Since the fracture strength of a material can effect its thermal shock parameter, the density of all specimens was tabulated and plotted in the form of weight percent carbon addition verses percent theoretical density (Figure 4) . At the present temperatures and pressures, only samples containing 1 w/o carbon or less prove to have a percent theoretical density of 90% or greater. From past research and a review of the literature, it is known that as little as 10 volume percent porosity can cause as much as a 50% reduction in fracture strength. This degree of reduction in fracture strength will have an overbearing effect on any material's thermal shock parameter.

This data, coupled with the thermal shock data and experiments, indicates that the composite containing only 1 w/o carbon and 3 w/o tungsten fibers will have the best thermal shock resistance.

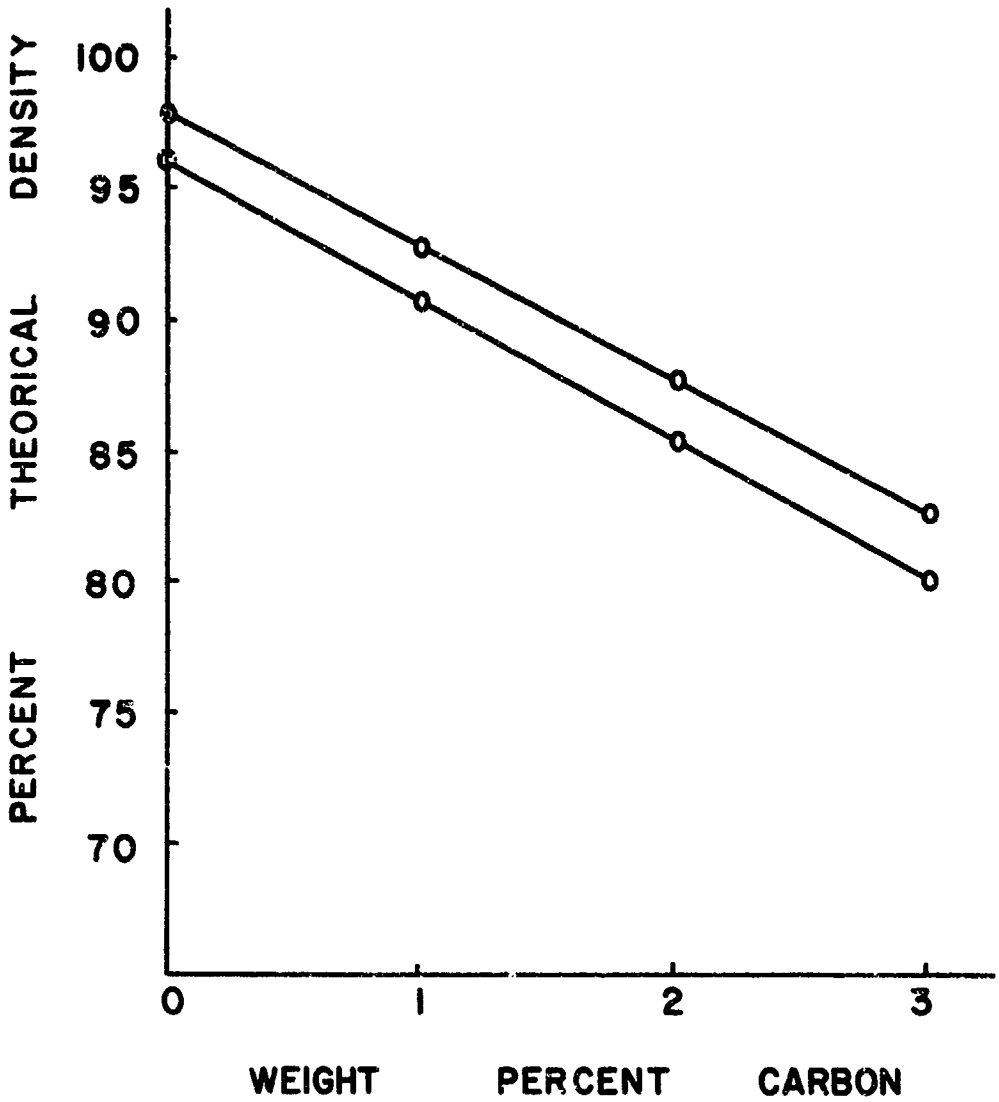


Figure 4. Percent theoretical density versus weight percent carbon additions for 3 w/o tungsten fiber (upper line) and 5 w/o tungsten fiber samples.

MICROPROBE AND METALLOGRAPHIC ANALYSIS

The ability of tungsten to form tungsten carbide when in the presence of free carbon has been known for sometime. The ability of the fibers in any composite to deform under severe loads is essential. Since tungsten carbide has an embrittling effect, a intense study of the tungsten fiber's composition after fabrication was undertaken. Specimens with the following composition were hot pressed at 2300°C under a loading of 8,500 psi.

3 w/o Carbon

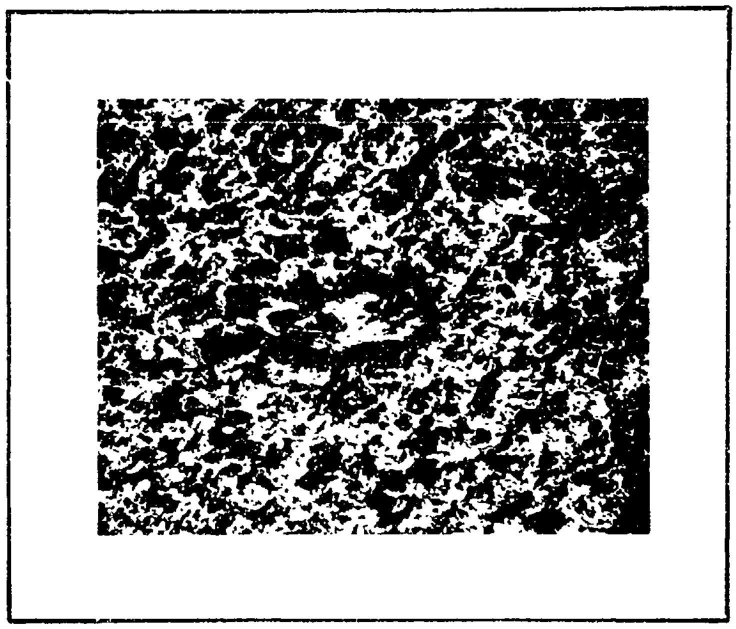
5 w/o Tungsten fiber

92 w/o Tantalum carbide

Each specimen contained 5 w/o tungsten fibers that had been alloyed with 0, 10, 15, or 25 percent Rhenium. After fabrication, each sample was metallographically polished using silicon carbide metallography paper and two stages of fine polishing using 0.3 and 0.1 micron AL_2O_3.

Optical examination of the sample containing the tungsten fibers with no alloying Rehnium is shown in Figure 5. The tungsten fibers were originally 0.005 in. in diameter. As is evident from the photographs, the tungsten fibers have been physically destroyed. Microprobe analysis verified the presence of tungsten carbide in large quantities. Further optical examination of specimen cross sections showed an area surrounding the tungsten fibers to be depleted of all carbon. This depleted area was on the order of twice the original diameter of the tungsten fibers.

Figures 6 and 7 are the specimens containing the tungsten fibers alloyed with 10 and 15 percent Rhenium respectively. As is optically



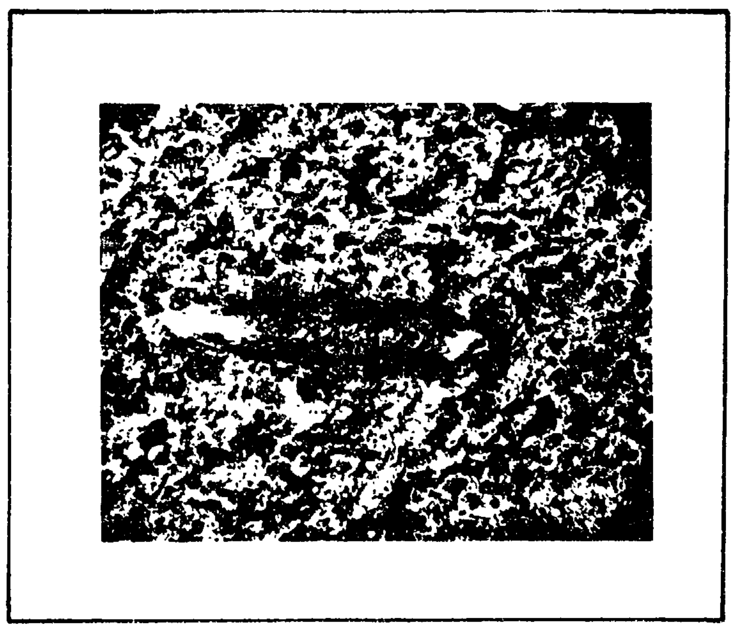


Figure 5. One hundred percent tungsten fiber in tantalum-carbide matrix with 3 w/o carbon addition after fabrication (150X).

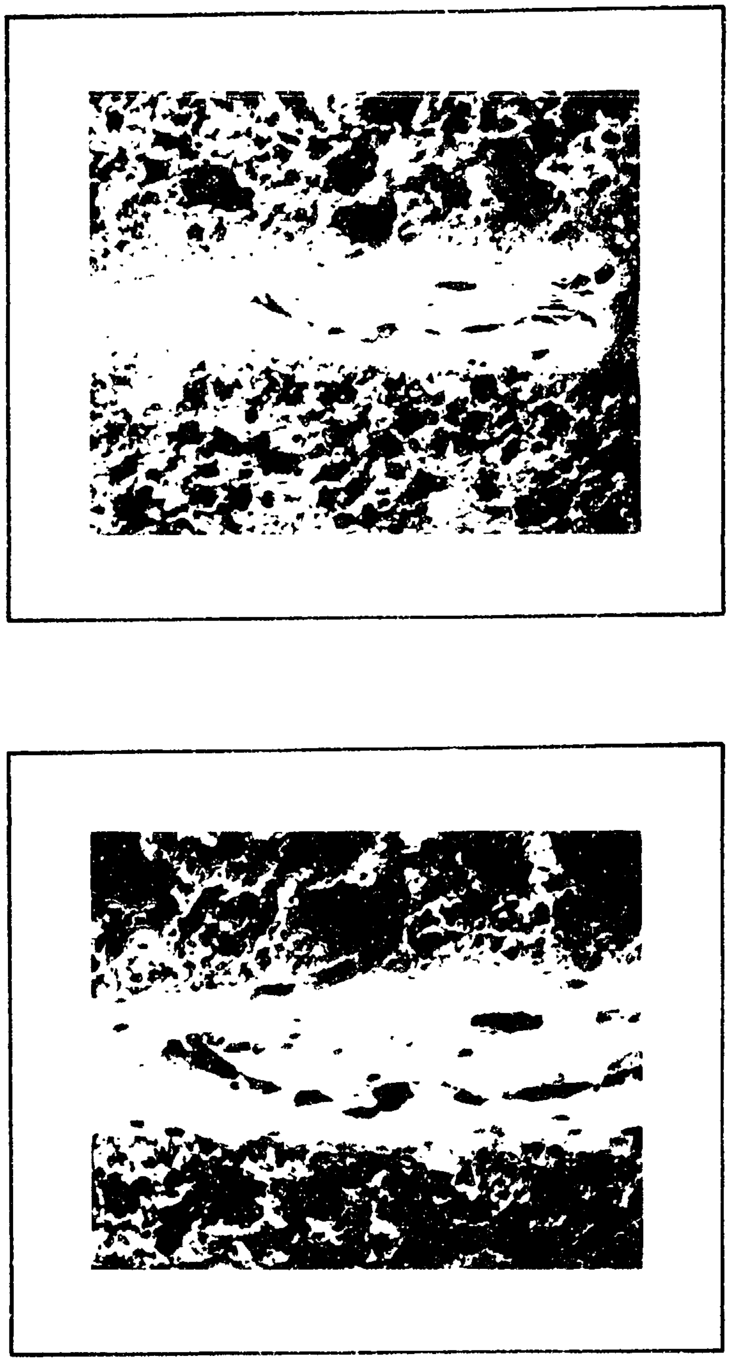


Figure 6. Ten percent Rhenium alloyed tungsten fibers in tantalum carbide matrix with 3 w/o carbon addition after fabrication (200X upper picture - 300X bottom picture).

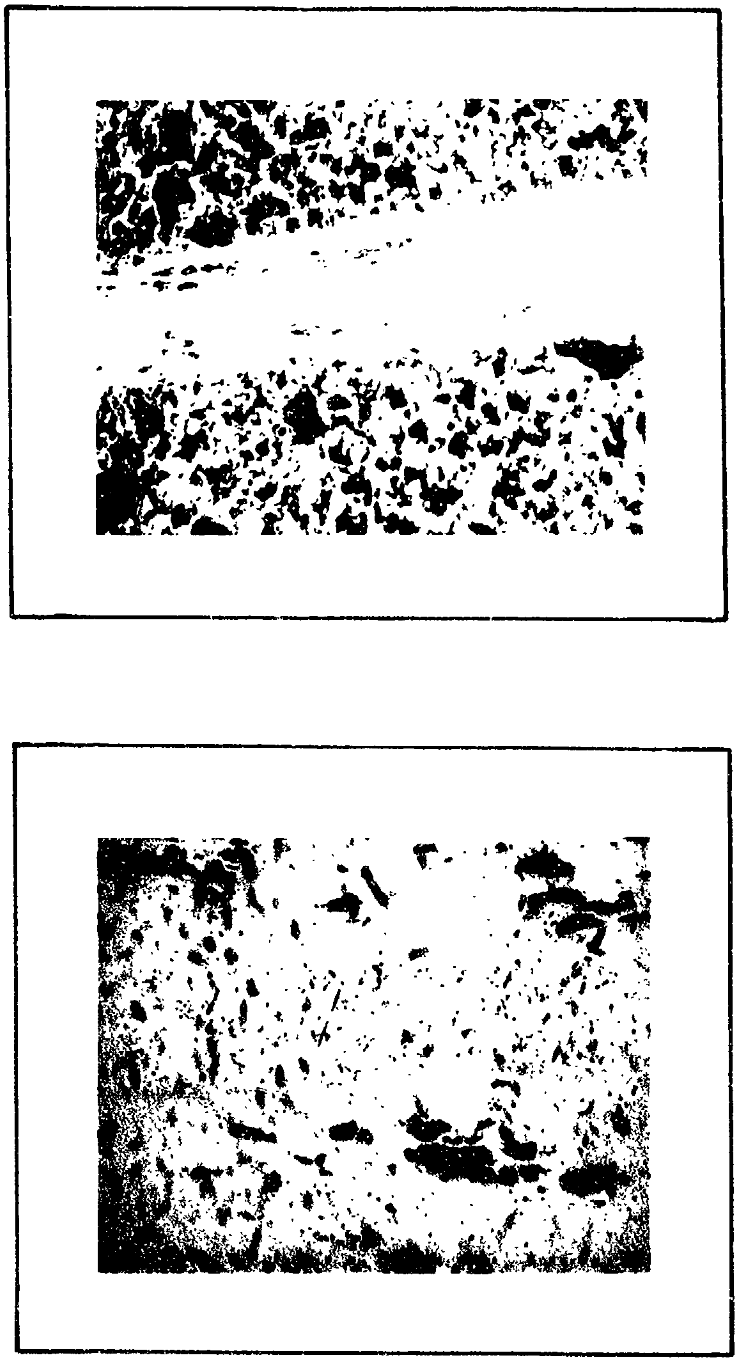


Figure 7. 15 w/o Rhenium alloyed tungsten fibers in tantalum-carbide matrix with 3 w/o carbon addition after fabrication (upper picture 225X - lower picture ~1000X).

evident the physical damage to the tungsten fibers has been reduced. Tungsten was found to be migrating from the center of the fiber to the tantalum carbide-tungsten interface and combining with the free carbon present in the matrix material to form tungsten carbide.

This was verified by use of the microprobe. Tungsten carbide was found on the surface of the tungsten fibers. However, it was in a reduced quantity when compared with the 100% tungsten sample.

The last specimen to be examined contained tungsten fibers that were alloyed with 25% Rhenium. Optical examination of this sample gave evidence of a second phase present on the surface of the tungsten fibers. Evidence was also present that indicated the diffusion of either or both tungsten and Rhenium from the center of the fiber in selected areas. An analysis by use of the microprobe indicated that there was no tungsten carbide present on or around the surface of the tungsten fibers. This data indicates that the tungsten fibers must contain 25% Rhenium to prevent the formation of tungsten carbide and embrittlement of the tungsten fibers. At this time the apparent second phase shown in Figure 8 has not been fully analyzed. However, it is felt that it is not an embrittling phase and should not hender the deformation ability of the tungsten fibers during loading under thermal shock conditions.

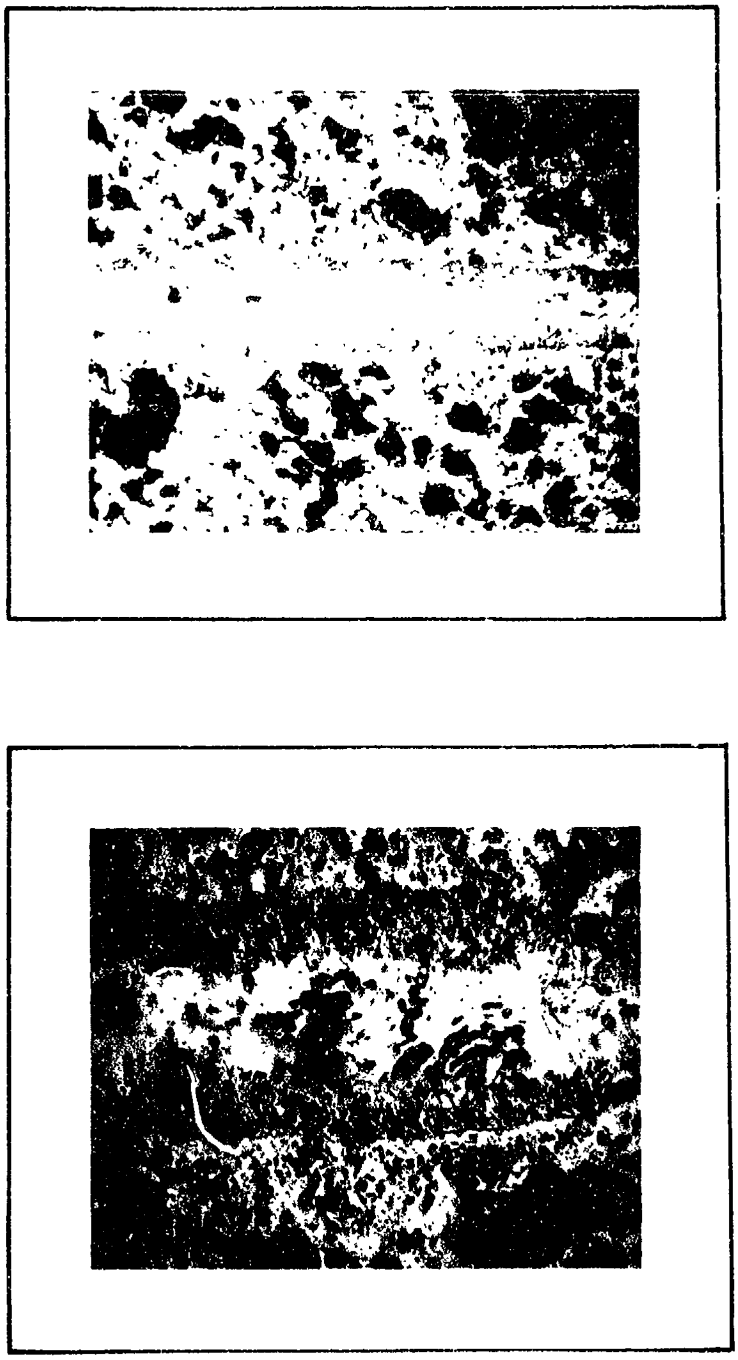


Figure 8. 25 w/o Rhenium alloyed tungsten fibers in tantalum-carbide matrix with 3 w/o carbon addition after fabrication (upper picture 150X - lower picture 400X).

EQUIPMENT

At present, the 50 KW Tocco has been set up and test run. During the testing, 35 KW was obtained and maintained. The procurement of a variable step ratio transformer has been made and is being installed. This piece of equipment will allow the tuning of the induction power supply to the induction coil without the manufacture of a new coil. This transformer should be installed as soon as a necessary water supply for cooling is obtained.

PROPOSAL FOR FUTURE WORK

1. Fabrication of HfC specimens and testing to obtain the composition with the optimum thermal shock resistance.

2. Test tantalum carbide specimens under plasma gas stream for thermal shock resistance and erosion.

3. Obtain densities, Young's Modulus, and compressive fracture strength of HfC composites.

4. Test fabricate full size rocket nozzle out of TaC to minimize fabrication problems and insure optimum properties.

CONCLUSIONS

1. In order to survive the temperature difference and thermal shock associated with solid propellant rocket nozzles, the composite must contain both free carbon and tungsten fibers.

2. The density of the material developed must be greater than 90 percent theoretical density in order to have the necessary strength to obtain a high thermal shock resistance parameter.

3. The tungsten fibers must be alloyed with 25% Rhenium or greater to prevent the embrittlement of the fibers by the diffusion of the free carbon in the matrix material and the formation of tungsten carbide.